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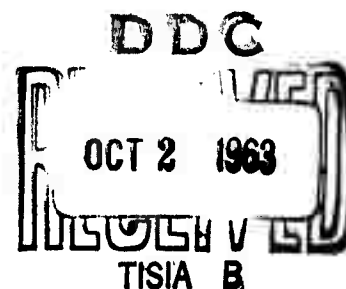
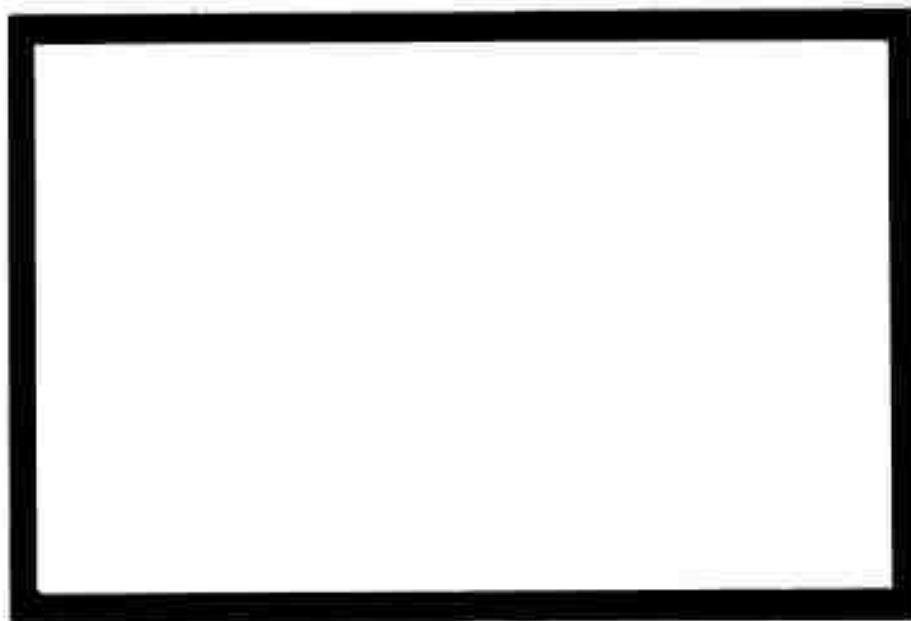
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~~AFOSR 62-99~~

UNIVERSITY OF UTAH

DEPARTMENT OF CHEMICAL ENGINEERING

~~AFOSR 62-99~~

Technical Report

on

IGNITION AND COMBUSTION OF SOLID PROPELLANTS

Under Air Force Grant ^{AF AFOSR} 62-99

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SUMMARY

This report summarizes work performed under Air Force Grant AFOSR 62-99. An extension of the thermal theory of ignition is presented, in which it is postulated that ignition occurs as a result of an exothermic surface reaction with the rate of this reaction being exponentially dependent on the solid surface temperature. This simple theory adequately explains the ignition data presented with respect to the effect of surface heat flux, initial propellant temperature, and pressure on the ignition process.

Radiation furnace tests have shown that the ignition time of a PBAA-AP propellant which contains a small amount of copper-chromite burning-rate catalyst is significantly less than the ignition time for the uncatalyzed propellant under the same conditions. Extinguishment tests of burning propellants subjected to rapidly decreasing pressure indicate that extinction occurs primarily as the result of gas velocity parallel to or normal to the surface. Decrease of pressure alone was not effective in quenching the burning of stable propellants.

I. INTRODUCTION

The ignition characteristics of composite propellants have been studied in a continuing research program at the University of Utah. This work was initially sponsored under Air Force Office of Scientific Research Contract AF 49(638) - 170. The work described in this report was supported under Air Force Grant AF-AFOSR 62-99, and additional research is being continued under Air Force Grant AF-AFOSR 40-63.

In the initial phases of this research, the response of several selected composite propellants subjected to surface heat fluxes was experimentally studied. The surface propellant samples were subjected to thermal-radiation heat fluxes from 1 - 13.5 cal/sec cm² and convective heat fluxes from 30 - 100 cal/sec cm². Parallel theoretical studies, which were guided by the experimental results, have given a satisfactory explanation of the general character of the ignition process. The scope of this research work has been broadened to include several phases of the combustion of solid propellants. Studies of burning propellant extinction, flame spread across the propellant surface, and fuel-binder pyrolysis reactions have been included in the work.

The following report includes a section on a proposed mechanism and theory of solid propellant ignition. A discussion of the experimental work conducted under AFOSR 62-99 is included and is organized according to the apparatus used in the work described. A short appendix concerned with the thermal properties of the propellants used is included.

II. THERMAL THEORY OF IGNITION

The basic feature of thermal theories of solid propellant ignition is that the rate of ignition process is controlled by a solid temperature, usually the surface temperature. The theories of Altman [1] and Hicks [2] represent early work in this area and revolve about considerations of propellant temperature. The advantage of the thermal theory approach is that the ignition process can be interpreted in terms of modifications of the transient forms of the heat conduction equation; and while the resulting equations are nonlinear, numerical solutions are easily obtained and generalization of the results of the numerical calculations is usually possible.

In the work described below, some additional consideration is given to the thermal ignition theory. It is assumed that the temperature of the propellant can be described by the following differential equation:

$$\rho c \frac{\partial v}{\partial t} = k \frac{\partial^2 v}{\partial x^2} \pm A e^{-E_a/Rv} \quad (1)$$

The initial and boundary conditions to be applied are:

$$\text{For } t = 0, \quad v = v_0.$$

$$\text{For } t > 0 \text{ and } x \rightarrow \infty, \quad v = v_0,$$

$$\text{For } t > 0 \text{ and } x = 0,$$

$$-k \frac{\partial v}{\partial x} = f_s \pm B e^{-E_b/Rv} \pm C e^{-E_c/Rv}. \quad (2)$$

Here x is the distance into the propellant; t is time; v is absolute temperature; k , ρ and c are respectively the propellant thermal conductivity, density and heat capacity. E_b and E_c are activation energies; and A , B and C are obtained from frequency factors and heats of reaction. In order to reduce the number of parameters to be handled, Equations (1) and (2) were put in dimensionless form by means of the substitutions

$$f_s = BF$$

$$v = \frac{E_b}{R} U$$

$$X = k \left(\frac{E_b}{RB} \right) x$$

$$t = \left(\frac{E}{RB} \right)^2 \Gamma^2 T$$

$$\frac{E_a}{E_b} = D$$

$$\frac{E_c}{E_b} = E$$

$$\frac{C}{B} = E_2$$

$$\frac{AkE_b}{RB^2} = D_2$$

In terms of dimensionless quantities, Equations (1) and (2) become:

$$\frac{\partial U}{\partial T} = \frac{\partial^2 U}{\partial X^2} + D_2 e^{-D/U} \quad (3)$$

For $T = 0$, $U = Y$.

For $T > 0$ and $X \rightarrow \infty$, $U = Y$.

For $T > 0$ and $X = 0$,

$$-\frac{\partial U}{\partial X} = F + B_2 e^{-1/U} + E_2 e^{-E/U} \quad (4)$$

Numerical solutions to these equations have been obtained for several values of the parameters. Normally only one or, at most, two exponential terms have been considered. Values of the dimensionless parameters were selected to be representative of experimental ignition data and to extend an order of magnitude above and below measured values.

Some justification and interpretation of these equations is in order. Equation (1) is the normal one-dimensional heat-conduction equation for homogeneous bodies with the inclusion of a term for an Ahrennius reaction added. This equation is discussed by Hicks [2]. All solutions have been made with an

assumed constant initial propellant temperature (v_0 or Y) and for an assumed semi-infinite body. Only constant flux heating at the surface of the propellant was considered. Most heating processes can be adequately approximated by a constant flux, and the assumption of constant surface flux results in a minimum number of problem parameters. Except when noted, the surface heat flux was assumed to be maintained until ignition occurred. The exponential terms in the boundary-condition equations would correspond to endothermic or exothermic reactions near or at the surface which result in a temperature-dependent change in the heat flux at the surface. The coefficients B and C in Equation (2) include the effect of energy feed-back efficiency to the surface and could conceivably be pressure dependent. The important point is that all temperatures are solid propellant temperatures. No effect of solid regression has been considered to this time.

Because of known facts about solid propellant ignition and the magnitudes of the activation energies of chemical reactions, certain conclusions can be drawn with respect to the propellant and surface reactions without solving the equations.

1. If two independent surface reactions are both to be important near the ignition temperature, and if one reaction is exothermic and one is endothermic, the exothermic reaction must have the higher activation energy. This results because the solid temperature is rising and when a high-activation energy reaction becomes important it quickly dominates the process. If propellant ignition is to occur, an exothermic reaction must eventually dominate. Normally, endothermic reactions have high-activation energies and exothermic reactions lower-activation energies, and thus the assumption of independent reactions does not appear to be very likely.
2. If endothermic and exothermic reactions are assumed to be coupled such that the rate of the exothermic reaction is proportional to the rate of the endothermic reaction, a reasonable possibility is found. If f_1 is the surface flux resulting from the endothermic reaction and f_2 the flux from the exothermic reaction, then at the propellant surface

$$f_1 = - B_1 e^{-E'/Rv} ,$$

and

$$f_2 = C_2 e^{-E''/Rv} = G_2 e^{-E''/Rv} e^{-nE'/Rv},$$

where n is the order of reaction of the products of the endothermic reaction. The total surface heat flux, f_t , is $f_s + f_1 + f_2$ or

$$f_t = f_s + G_2 e^{-(E' + E'')/Rv} - B_1 e^{-E'/Rv}.$$

In this fashion, the apparent activation energy of the exothermic reaction is $nE' + E''$ and is always greater than the activation energy of the endothermic reaction. If $E'' \ll E'$, the surface reactions can be treated as a single reaction, provided B_1 is less than G_2 .

Equation (3) was put into finite difference form and numerical solutions were obtained by a modified Schmidt method. Because the surface flux varied rapidly with time as the surface reactions became important, the temperature at the fictitious point at $X = -\Delta X$ was calculated from the following equation:

$$U(-1, N) = U(1, N) + 2\Delta X \left\{ F(0, N) + \frac{1}{2} [U(0, N+1) - U(0, N)] \frac{\partial F}{\partial U}(0, N) \right\} \quad (5)$$

where the first symbol in the parenthesis refers to the position ($X=0$ is the surface) and the second symbol refers to the time increment. (See reference 3, p. 475.) Equation (5) effectively evaluates the surface flux at time $((N+1)/2)\Delta T$. Ignition was assumed to have occurred when the surface temperature was rising very rapidly. At the ignition time, the surface temperature was approximately doubling during each increment of time. In the calculations 100 to 200 time increments were used. Analytical solutions to the linearized form of Equation (3) were used to calculate the temperature profile until the flux from surface reactions was about 5 per cent of the external flux.

The range of the variables considered was determined on the basis of experience with composite propellants. An attempt was made to consider only reasonable conditions in an attempt not to obscure useful generalizations which would not apply to unreasonable conditions. Table I gives the range of dimensionless variables considered.

Several computer runs were made in which only an exothermic reaction in the propellant was considered. These runs correspond to the solutions reported by

Hicks and were made to obtain a check against his results. Adequate agreement was obtained. In the remainder of the runs, the parameter D_2 in Equation (3) was set to zero and only surface reactions were considered. Since this work was anticipated to be of a more or less exploratory nature, it was felt that the study of the more easily interpreted surface-reaction case would be more informative. Even in the case of a reaction throughout the body of the propellant, the energy would be released very near the surface. Quantitatively, at least, the surface and body reaction cases should be very similar. Also, because a relatively slow computer (IBM 1620) was used in the calculations a significant saving in time was achieved by considering just the surface reaction, since an exponential needed to be evaluated only once per time interval.

In the numerical solutions of Equations (3) and (4), the following conditions were considered:

1. The effect of surface flux, activation energy and initial temperature on ignition time was considered for a single exothermic reaction. In this case the parameters in Equations (3) and (4) D_2 and E_2 were taken to be zero. The effect of pressure on ignition times was implied by varying the coefficient B_2 in Equation (4) from a value of 1.0 to 0.1 and 10.0.
2. The effect of a surface endothermic reaction was considered by variations in the parameters E and E_2 . Parameter D_2 was set equal to zero.
3. Pulsed application of energy was considered by reducing the parameter F to zero at some time before ignition occurred.

The results of these calculations are discussed in the following section.

RESULTS OF COMPUTER CALCULATIONS

Exothermic Surface Reaction

Because of the choice of dimensionless parameters, the effects of the initial solid temperature and the reaction activation energy were related ($Y = \frac{R}{E} v_0$) as were the effects of surface flux and the coefficient B in Equation (2) ($F = f/B$). Figure 1 summarizes a typical set of calculations and shows the effect of the dimensionless flux on the dimensionless ignition time for various values of the dimensionless initial temperature. In all cases, these lines were essentially straight and the slope of the lines were slightly

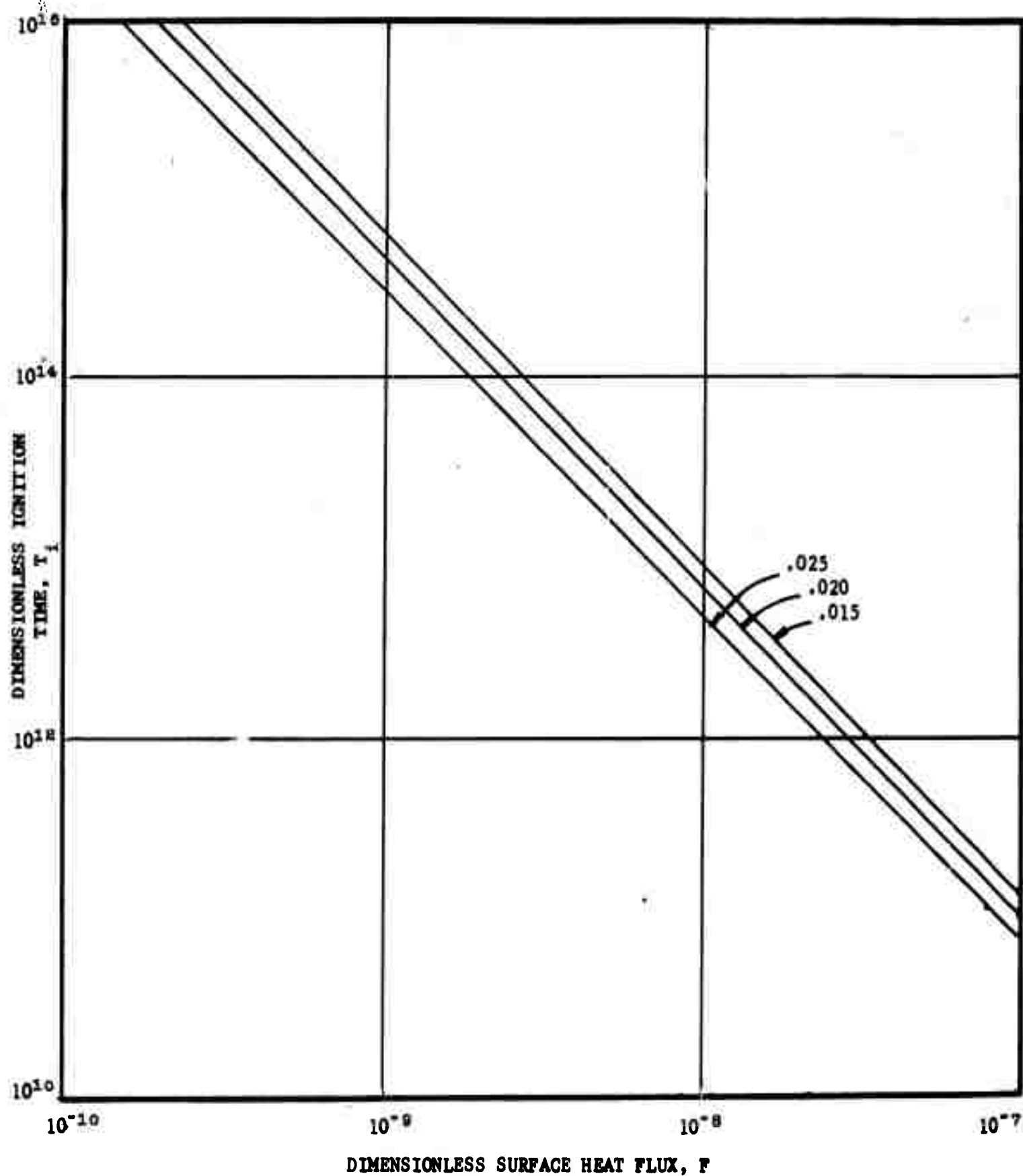


Figure 1. A typical plot of calculated ignition time versus surface heat flux. The parameters on individual lines are the dimensionless initial propellant temperatures. These results are solutions to Equations (3) and (4) with $D_2 = E_2 = 0$, $B_2 = 1.0$.

greater than minus one. Figure 2 shows the slope of the $\log T_1^{\frac{1}{2}}$ versus $\log F$ plotted as a function of the parameter Y . The slopes approach minus one as the activation energy increases (Y decreases). The slopes decrease by 1 to 2 per cent as the surface flux was increased by one or two orders of magnitude. The linearly estimate surface temperature at ignition U_1^L calculated as

$$U_1^L = 2F \left(\frac{T_1}{\pi} \right)^{\frac{1}{2}} + Y$$

was found to be almost completely independent of the parameter Y for a constant surface heat flux. This fact is illustrated in Table II. For a given propellant, this corresponds to changing the initial propellant temperature, and the independence of the linearly calculated surface temperature at ignition on initial propellant temperature has been observed experimentally [4]. By making use of the independence of U_1^L of Y , the numerical data can be correlated in a manner similar to the technique for experimental data, and the numerically calculated results can be summarized in a single equation. The numerical calculations for the case of a single surface reaction with parameter B_2 equal to one can be summarized in the following equation:

$$T_1^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}}}{2F} \left(\frac{1}{1 - 2.40 \log_{10} F} - Y \right) \quad (6)$$

The maximum difference in calculated ignition times between the numerical calculations and Equation (6) is about 10 per cent. The maximum error occurs at high values of Y . At low values of Y the agreement is almost exact.

If the thermal ignition model is essentially correct, the effect of pressure on the ignition time can be interpreted as a change in the parameter B_2 in Equation (4) since this parameter characterizes the rate of the surface reaction and the feed-back of energy. Computer runs were made with values of the parameter B_2 equal to 0.1, 1.0 and 10.0 for the same values of flux and at the same initial temperature. The slopes of the $\log T_1^{\frac{1}{2}}$ versus $\log F$ lines were found to be independent of the factor B_2 . From these results it was found that the dependence of T_1 on B_2 can be approximated to give

$$T_1 \propto B_2^m \quad (7)$$

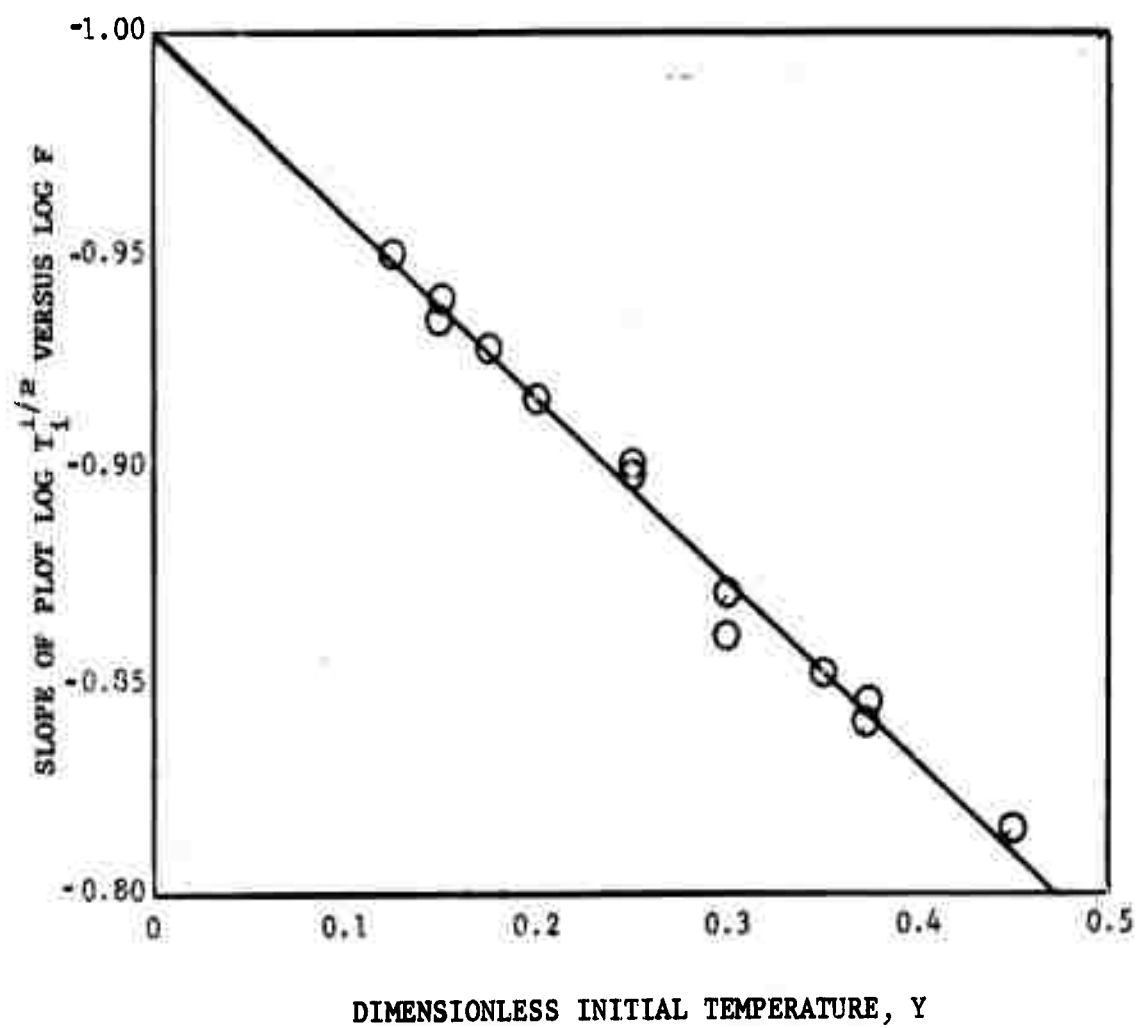


Figure 2. Calculated slope of $\log T_1^{1/2}$ versus $\log F$ plot as function of initial temperature, Y . This slope is a weak function of F , and the line represents the best fit to the calculated slopes.

where the exponent m is almost independent of the surface flux and varied from .13 to .32 as Y varied from .015 to .0375. Table III summarizes the results of these runs. If the parameter B_2 is assumed to be directly proportional to the pressure, an effect of pressure on ignition time is about equal to the effect of pressure on steady burning rates. The theoretical effect of pressure is about equal to the experimental values previously reported [4] [5]. Universal agreement on the effect of pressure on ignition is not, however, to be found in the literature [5].

Endothermic and Exothermic Surface Reactions

A short series of computer runs were made in which a surface endothermic and a surface exothermic reaction were considered. Values of the parameter E of 0.5 and 0.8 were considered which correspond to the ratio of the effective endothermic to exothermic reaction activation energies. The parameter E_2 (assumed negative) was varied systematically from values in which the endothermic reaction contributed negligible surface flux at the ignition time to such a large value that ignition could not occur. Figure 3 summarizes the results of these calculations. It appears that an endothermic reaction could have important but not dominant effect in the ignition reaction only if the parameter E_2 happens to be just the right value. A range of about five is all that is of importance. Also the effect of the endothermic reaction would be very strong at low heat fluxes and negligible at high heat fluxes. In this case the slope of the $\log T^{1/2}$ versus $\log F$ line varies from $+\infty$ at very low fluxes to approaching minus one at high fluxes. Because experimentally observed data do not indicate such a trend, and because it is unlikely that two reactions would occur to give a value of E_2 in the very narrow limits of importance, it is unlikely that an endothermic reaction that is not followed immediately by a rapid exothermic reaction is important in ignition.

Pulsed Application of Energy

In the previous computer runs discussed, the surface flux was maintained until ignition occurred. A series of computer runs were made in which the externally applied surface flux was reduced to zero some time before ignition occurred. Table IV summarizes the results of these calculations for a typical set of conditions. It was found that if the external heat flux were stopped

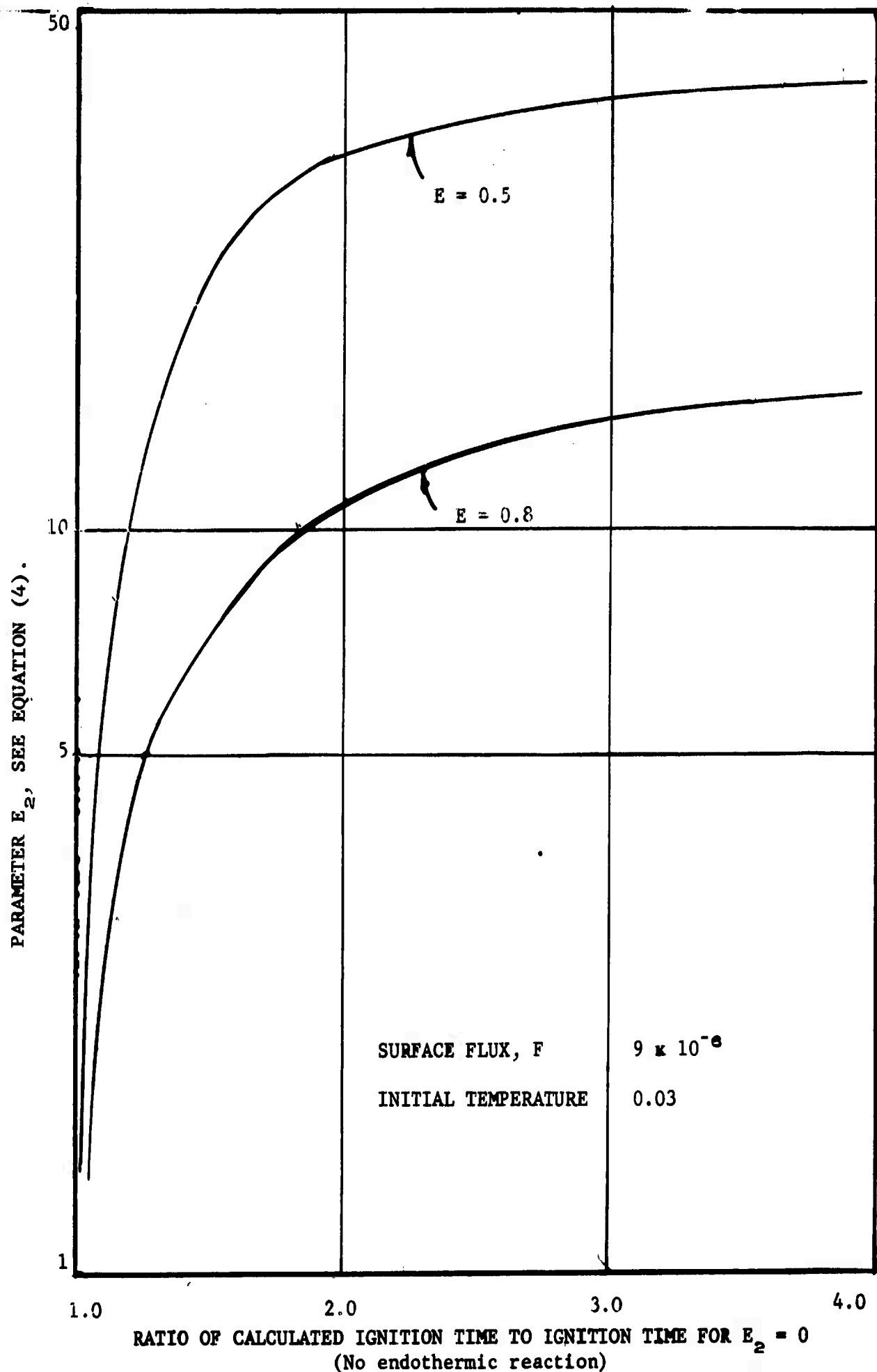


Figure 3. The effect of a surface endothermic reaction on calculated propellant ignition times. The parameter E , the ratio of endothermic to exothermic reactions activation energies from Equation (4), is shown on individual curves. The ordinate values of the parameter E_2 should be multiplied by 10^{-4} for E equal to 0.5 and by 10^{-2} for E equal to 0.8.

before the surface flux from reaction became greater than the externally applied flux, ignition did not occur, at least in a period 10 to 20 times as long as the period for energy application. The difference between the time when ignition occurred after discontinuation of the external flux and the ignition time for continuous application of flux was only 1 to 2 per cent of the continuous flux ignition time. If this thermal ignition model is adequate, it appears that for all practical purposes, the results of ignition tests by pulse heating and by continuous application of energy must be equivalent.

An exception is easily conceived. If, in preliminary phases of the ignition process and after cessation of external flux, a considerable volume of self-combustible gases are generated, then confined so that, in time, they would ignite spontaneously, the energy so released might provide enough energy for completing the ignition process. It is in arc-image experiments, with their small, pressurized sample chambers, that this phenomenon is most likely to occur. Arc-image ignition data of the delayed (after external flux) ignition type would be expected to be strongly dependent on size and shape of the sample chamber.

III. RADIATION FURNACE TESTS

Ignition tests were made in the atmospheric radiation furnace. Figure 4 shows a side section of this apparatus. Additional information concerning this furnace can be found in previous reports from this laboratory. Table V and Figure 5 present the results of recent work. In these tests two propellants designated F and G were used. Table VI summarizes the properties of these propellants, and shows that the F propellant only contained a copper-chromite burning-rate catalyst. It was found that the ignition times of the catalyzed F propellant were the same as had been observed with other catalyzed propellants at low flux levels and were only about two-thirds the ignition times of the uncatalyzed G propellant under the same furnace conditions. Apparently the burning-rate catalyst exerts a very great influence on the ignition process. At high flux levels the ignition times for the F propellant were longer than other catalyzed propellants, but recent data indicate that this effect may be caused by transmissivity of the F (and G) propellant.

Ignition data previously presented concerning the effect of pressure on ignition in the sealed, low-temperature radiation furnace were correlated in terms of furnace radiant flux [4]. At low pressures, the heat flux resulting from free-convection transfer from hot gases in the furnace to the propellant surface is negligible when compared to the radiant heat flux. At the high pressures, some effect of free convection should be noted, particularly at the low furnace temperatures. Although recent theories have appeared concerning transient, free-convection heat transfer [7] [8], it was doubtful that these results would apply in the peculiar geometry of the radiation furnace. Tests were made to determine the transient free convection coefficients. Unshielded heat-flux gages were mounted on the sample injection rod and thrust into the furnace. The time-surface temperature history of the heat-flux gage was obtained while the gage was in the furnace, and the time-surface temperature data were converted into time-heat flux data. Tests were made at various furnace pressures. It was assumed that no free convection was present under vacuum, and the difference between vacuum tests and pressure tests at the same furnace temperature was attributed to free-convection heat transfer. Table VII summarizes the data as does Figure 6. Table VII also shows the apparent absorptivity of the heat-transfer gages as a function of the incident

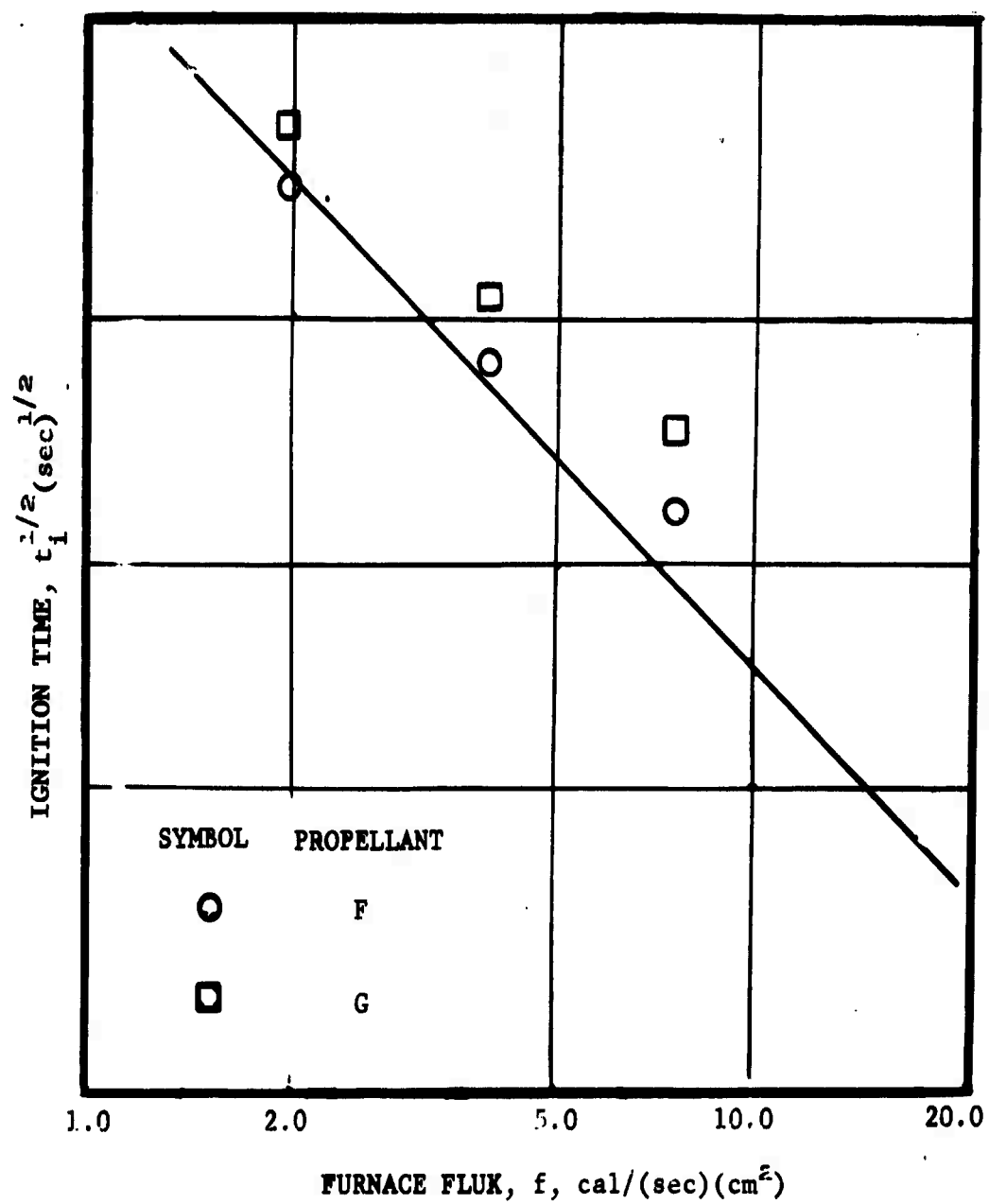


Figure 5. Propellant ignition data from the atmosphere radiation furnace. The solid line gives the best fit for all catalyzed AP propellants previously tested [4].

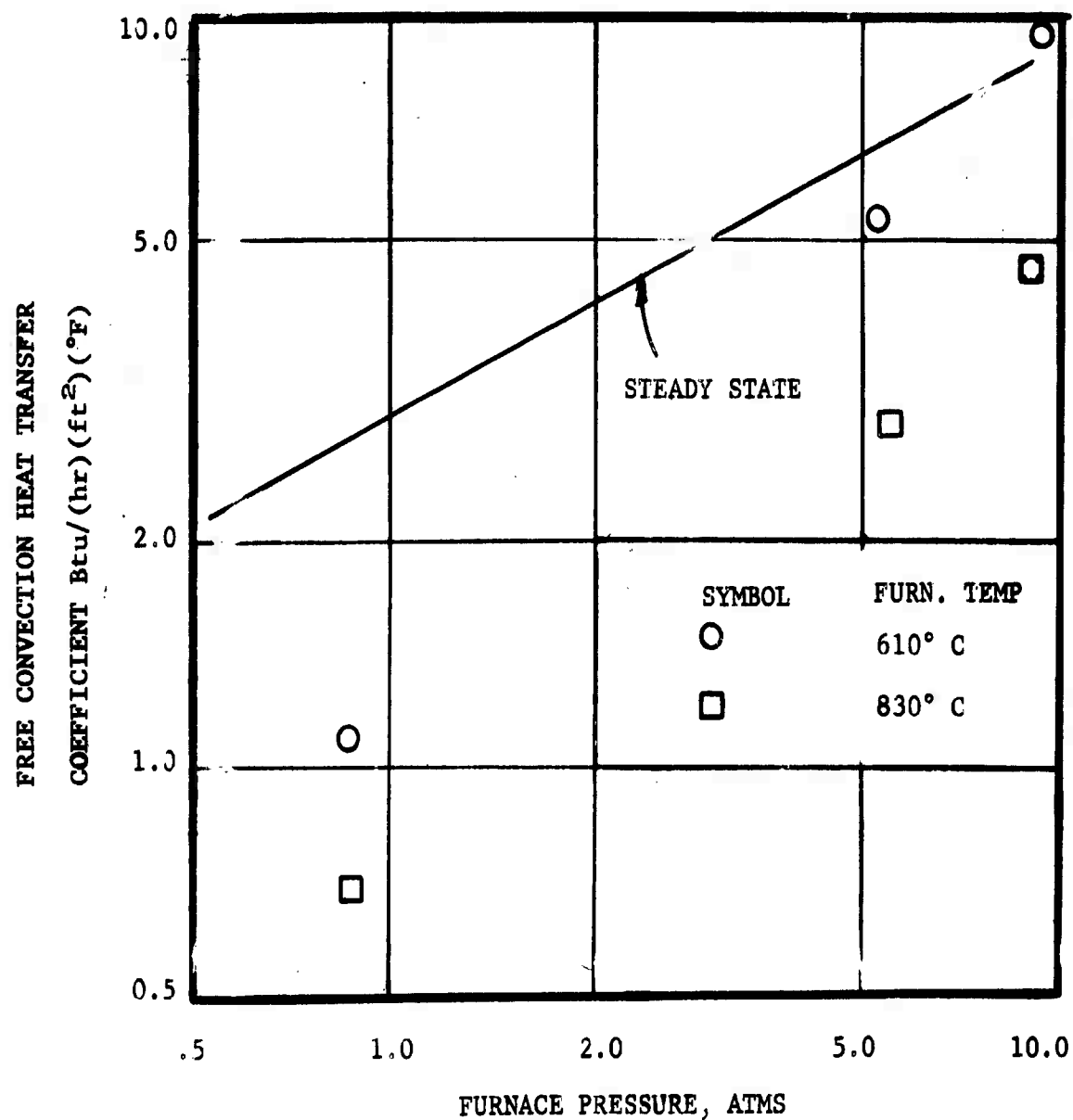


Figure 6. Comparison of measured transient heat-transfer coefficients to calculated steady state values [10].

radiation temperature. The variation is about what would be expected of a refractory surface in this temperature range [9].

The measured free-convection heat-transfer coefficients were significantly lower than the values calculated from steady-state measurements at low pressures. (See Figure 6.) The high-pressure data tend to approach the calculated steady-state values. The free-convection heat transfer in the radiation furnace seems to be quite complex. However, it appears that neglect of free convection at low pressures is entirely justified. If the previously reported data on the effect of pressure on ignition at low fluxes is corrected for free-convection effects, the conclusion that pressure does not have a great effect on ignition at low fluxes is still valid.

Preliminary tests were made in the radiation furnace to evaluate a technique for determining the pyrolysis properties of fuel-binder polymers. In this work, a thin layer of polymer is cured onto the surface of a thin-film heat-transfer gage; the polymer surface is then exposed to thermal radiation; and the measure-time-surface temperature history of the gage is used in conjunction with the surface heat flux and the thermal properties and thickness of the polymer film to infer the character of the polymer-pyrolysis reactions. This work will be continued first employing the radiation furnace and later the shock tube.

IV. SHOCK TUBE TESTS

Research on ignition of propellants in the shock tube was concerned with the role of propellant ingredients. The following variations in propellant composition studied were: (1) the particle size of ammonium perchlorate, (2) loading of perchlorate in propellants, and (3) materials added to propellants to modify burning characteristics. The polymer system used was a polybutadiene-acrylic acid copolymer cured with an epoxy-type curing agent.

Considerable effort has been devoted to developing a procedure for preparing propellant samples for testing. In earlier ignition studies, propellant samples were all prepared by cutting solid cylinders of propellant from large slabs or rods of propellant, and then the propellant was cemented into the sample holders. This technique for preparing propellant for testing was the only method that could be used before equipment for processing propellant became available. Propellant, freshly prepared, was more recently cast directly into the sample holders and cured in place. The propellant surface was carefully cut with a sharp razor blade immediately before testing. Ignition tests on the two types of propellant samples of the same composition showed that samples made by casting of propellant into holders gave more consistent ignition times. Samples prepared by cutting solid cylinders from slabs gave nearly the same ignition times, but the data are more scattered and tend to give shorter ignition times. It is suspected that during the cutting of samples from slabs, perchlorate particles were separated from the polymer. This provided a slight defect for faster ignition by convective heat transfer.

In the preparation of large propellant grains by casting propellant around a mandrel in the rocket chamber, the propellant surface after pulling the mandrel appeared to have a fuel-rich (polymer-rich) surface. In an attempt to simulate this effect on a small scale, samples of propellant were made in which the surfaces were smoothed before curing. This technique produced a surface on which all particles of perchlorate were covered with a thin polymer coating. Ignition tests on these samples of propellant in the shock tube showed that ignition times were of the order of 15 to 20 per cent longer than for propellant with freshly cut surfaces. Figure 7 summarizes these results.

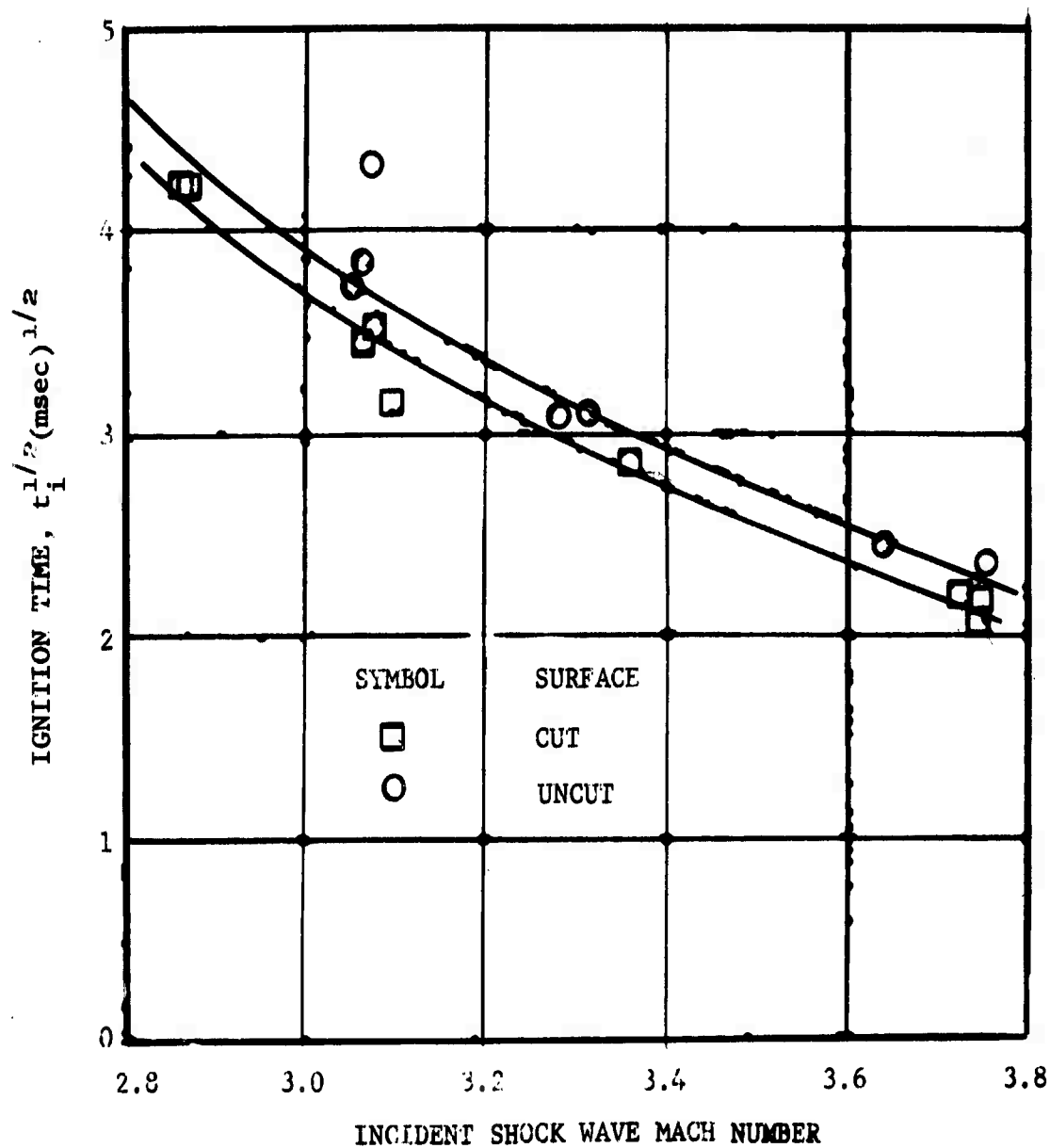


Figure 7. A comparison of ignition times for samples with fresh cut surfaces to samples with as cast, polymer rich surfaces. The pressure at the sample was 350 psig. The ratio of section area at sample to flow control orifice area was about four to one.

V. RAREFACTION TUBE STUDIES

The design and fabrication of a new rarefaction tube has been completed. This tube is of 1.900-inch inside diameter and has flanged sections permitting the assembly of lengths from two to twenty feet. Particular care was taken during machining to give a smooth and near-uniform bore. A discussion of the theory and operation of the rarefaction may be found in reference [4].

Extinguishment Tests

Approximately 200 runs were made to explore possible effects of pressure transients upon the burning of solid propellant strands. In these tests, a $\frac{1}{2}$ -inch diameter strand was mounted in the head end (closed end) of the tube, the center lines of the tube and strand coinciding. The burning strand was viewed through a quartz window in the tube wall by either a photocell or by means of high-speed photography. The pressure history was obtained from pressure transducers mounted in the tube wall. The tube was first evacuated and then pressurized with nitrogen gas to prevent gas phase reactions between the propellant ignition products and ambient oxygen. Nozzles giving pressure drops of 11 to 74 per cent of the initial pressure in the tube were used. Three propellants, designated as F, M, and H, were used in the tests, each composed of a polybutadiene-acrylic acid copolymer binder, ammonium perchlorate oxidizer, and copper chromite catalyst. The burning rates were in the order $F > M > H$.

The early runs were made with strands which extended $\frac{1}{2}$ -inch to 1-inch from the surface of the sample holder. With such samples it was possible to quench each of the three propellants under suitable tube conditions. Under less severe conditions the flame, as indicated by the photocell signal, appeared to be partially quenched during the passage of the rarefaction and then recovered during the subsequent interval of constant pressure. It was later learned that this behavior was caused almost entirely by the gas velocity during the rarefaction, rather than the pressure drop. The maximum velocity at a point 1-inch from the closed end of the tube during the passage of a rarefaction was about 200 fps for these tests. The angle between the burning surface and the tube axis also appeared to affect the transient behavior of the flame.

In later runs with the surface of the strands cut approximately flush with the closed tube end and perpendicular to the tube axis, it was possible to quench only the slow burning H propellant although the pressure decreased at a rate greater than 100,000 psi/sec. It appears the propellant extinction occurs by gas flow across or normal to the surface, and it is not simply related to the rate of pressure decrease.

Flame Spread and Ignition

An investigation is in progress to study ignition under conditions which more closely approximate those present in a rocket motor than do the conditions of much previous work. The experimental apparatus consists of a sample holder mounted in a transparent section of a tube in which a condition of constant pressure and gas velocity can be maintained. Two rectangular slots were machined in the flat top surface of the holder, in which two flush-mounted propellant samples, at present $1/8 \times 1/8 \times 1\frac{1}{2}$ -inch, can be placed with their long dimension perpendicular to the direction of flow. Several holders, with separation distances between the slots ranging from $\frac{1}{2}$ -inch to 2-inch, have been used. The upstream sample is ignited, the gas flow started, and the ignition of the downstream sample observed through the use of a photocell or high-speed photography.

The initial tests, conducted at atmospheric pressure and low gas velocities, were sufficiently encouraging that the rarefaction tube used in the pressure transient tests was modified to permit its use in this work. This made it possible to operate at pressures of several hundred pounds per square inch and Mach Numbers of up to about 0.5. Work is continuing to sufficiently refine the techniques to yield reproducible results.

APPENDIX A.

THERMAL PROPERTIES OF COMPOSITE PROPELLANTS AND
THEIR CONSTITUENTS

The densities, heat capacities and thermal diffusivities of the several composite propellants used in these studies, the various fuel-binder polymers of interest and of ammonium perchlorate were evaluated from published data or by physical measurement. The measurement techniques are discussed below. Table VI summarizes the thermal properties of these materials; Table VIII gives their chemical composition.

Density

Propellant and polymer densities were measured by water displacement. An experimental accuracy of ± 2 per cent is anticipated.

Heat Capacity

The heat capacities of propellant and polymer samples were determined at room temperature by use of a Dewar-flask-calorimeter. The calorimeter was calibrated by means of copper bars of known heat capacity, and calorimeter temperature changes were recorded to the nearest $.01^{\circ}\text{C}$ with a Beckman differential thermometer. The initial sample temperature was approximately 95°C , and the final sample temperature was about 25°C . The anticipated accuracy is ± 3 per cent. The measured values of propellant heat capacities and the values calculated from the known composition and the heat capacities of the constituents differed by less than 3 per cent.

Thermal Diffusivity

An unsteady state technique was used to determine the thermal diffusivity of propellants, polymers and ammonium perchlorate. Cylindrical samples of these materials were prepared with fine thermocouples mounted in their geometric centers. These cylinders were quickly immersed in an agitated bath. The bath temperature was different from the initial cylinder temperature. The center temperature-time relationship was recorded and was used to calculate the sample thermal diffusivity in the manner described below. The samples of propellant and polymer were cast cylinders $1\frac{1}{2}$ inches in diameter and about 4 inches long.

The surface of the propellant samples was coated to prevent dissolution of the ammonium perchlorate in the water used in the agitated bath. The ammonium perchlorate samples were made by cementing together pressed cylindrical discs (99 per cent of theoretical density) 2.54 cm in diameter and .6 to .7 cm high to give cylinders 2.54 cm in diameter and 4 to 4.5 cm high. Carbon tetrachloride was used in the agitated bath in this case.

If a plot is made of the logarithm of the ratio of the difference between the cylinder center temperature and the bath temperature to the initial temperature difference against linear time, it is found that after a short time this plot becomes a straight line. During this period [3, p. 228]

$$\frac{v - v_0}{v_b - v_0} = C_1 \exp -\alpha t (\lambda_1^2 + \beta_1^2) \quad (A1)$$

where v , v_0 , and v_b are respectively the center temperature, initial temperature and bath temperature; α is the material thermal diffusivity; t is time and C_1 is a time-invariant constant. The constants λ , and β are respectively the smallest roots of the equations:

$$\lambda \ell \tan \lambda \ell = \frac{h \ell}{k} \quad (A2)$$

and

$$a \beta J_1(a \beta) = \frac{h a}{k} J_0(a \beta) \quad (A3)$$

where a is the cylinder radius, ℓ the half-cylinder height, k the solid thermal conductivity and h the surface heat-transfer coefficient between the solid and agitated bath (assume constant over the surface).

The surface heat-transfer coefficient was determined by immersing a 2.5 cm o.d. by 5 cm high copper cylinder in the agitated baths. In the case of copper, the terms $\frac{h \ell}{k}$ and $\frac{h a}{k}$ are so small that a limiting form of Equation (A1) can be used which neglects the temperature gradient in the solid. In the water bath h was found to be 0.104 cal/(cm²)(sec)(°C) and in the carbon tetrachloride bath h was found to be .025 cal/(cm²)(sec)(°C). Sample position and agitation was controlled to insure that these same values would apply in the thermal diffusivity tests.

In the case of the thermal diffusivity determinations on the propellants and the polymers, $\frac{h a}{k}$ and $\frac{h \ell}{k}$ were greater than 100, and the roots of Equation (A1) are $\lambda = 1.57$ and $\beta = 2.40$. These values are essentially independent of h or k , and the thermal diffusivity can be evaluated directly. In these tests,

the initial solid temperature was 95°C and the bath temperature 25°C.

In the case of ammonium perchlorate, the terms $\frac{h_l}{k}$ and $\frac{h_a}{k}$ range in value from 20 to 50, and λ_1 and β_1 had to be evaluated by use of the measure slope of the $\log (v - v_o)/(v_b - v_o)$ versus t plot and a trial and error solution. Values of the heat capacity and density were required to permit calculation of the thermal conductivity for use in Equations (A2) and (A3). In these tests, the initial ammonium perchlorate temperature was 0° to 5°C and the bath temperature was about 25°C. The anticipated error of the thermal diffusivity measurements is ± 2 per cent.

Thermal Conductivity

The thermal conductivity of the various materials was calculated from the equation:

$$k = \rho c \alpha$$

The measured thermal conductivities of the propellants were found to be within 3 per cent of the value calculated from the volumetric loading and the thermal conductivities of the constituents by use of the Maxwell equation [10].

APPENDIX B

TABLE NO. I

THE RANGE OF PHYSICAL PARAMETERS CONSIDERED
FOR COMPUTER CALCULATIONS

<u>Quantity</u>	<u>Symbol</u>	<u>Dimensions</u>	<u>Range</u>
Dim. Heat Flux ¹	F	none	$10^{-12} - 10^{-4}$
Dim. Initial Temp.	Y	none	.012 - .05
Dim. Ignition Time	T	none	$10^8 - 10^{20}$
Dim. Ignition Temp.	U_1^L	none	.03 - .07
Parameter Eq. (4)	E_2	none	.001 - 0.2
Parameter Eq. (4)	E	none	.5 and .8
Parameter Eq. (4)	B_2	none	.1, 1.0, 10.0
Activation Energy ²	E/R	°K	6000 - 25000
Linear Ignition Temp. ²	V_1^L	°K	600 - 900° K

1. These values were determined to make F the same order of magnitude as $\exp(-1/U_1^L)$. The parameter U_1^L can be calculated from E/R and V_1^L shown below.
2. These values assume an initial solid temperature of 300° K.

TABLE NO. II

VARIATION OF DIMENSIONLESS, LINEAR SURFACE
TEMPERATURE AT IGNITION, U_1^L , WITH SURFACE
HEAT FLUX AND INITIAL PROPELLANT TEMPERATURE

Surface Heat	<u>Dimensionless Initial Temperature, Y</u>							
<u>Flux, F</u>	<u>.0125</u>	<u>.0150</u>	<u>.0175</u>	<u>.020</u>	<u>.025</u>	<u>.030</u>	<u>.035</u>	<u>.0375</u>
3×10^{-4}						.1057		.1062
7×10^{-5}						.0910		.0916
6×10^{-5}					.0892	.0896	.0899	.0901
5×10^{-6}						.0728		.0735
9×10^{-8}					.0758	.0762	.0765	.0767
3×10^{-7}					.0600	.0604	.0606	.0609
6×10^{-8}		.0542		.0545	.0547			
5×10^{-8}		.0477		.0478	.0481			
4×10^{-8}	.0420	.0422	.0426	.0427	.0429			
2×10^{-11}	.0377	.0376	.0375					
2.5×10^{-12}	.0348	.0348	.0349					

TABLE NO. III

The effect of variation of the parameter B_2 in Equation (4) on calculated ignition times. The exponent m in the equation, $T_i \propto (B_2)^m$, is presented as a function of the surface heat flux and initial propellant temperature. The parameters D_2 and E_2 in Equations (3) and (4) were set to zero in these calculations.

<u>Dimensionless Initial Temperature, Y</u>	<u>Dimensionless Surface Heat Flux, F</u>	<u>Exponent, m</u>
.0375	5×10^{-6}	.302
.0375	7×10^{-5}	.320
.0375	3×10^{-4}	.354
.03	3×10^{-7}	.248
.03	5×10^{-6}	.258
.03	9×10^{-6}	.264
.03	6×10^{-5}	.288
.03	7×10^{-5}	.292
.03	3×10^{-4}	.317
.02	4×10^{-10}	.161
.02	5×10^{-9}	.168
.02	6×10^{-8}	.178
.015	2.5×10^{-12}	.123
.015	2×10^{-11}	.127
.015	4×10^{-10}	.134

TABLE NO. IV
CALCULATED IGNITION TIMES FOR THE CASE OF CONTINUOUS
APPLICATION OF ENERGY COMPARED TO IGNITION TIMES CALCULATED
FOR THE CASE OF PULSED APPLICATION OF ENERGY

Surface Heat Flux, F	4×10^{-10}	4×10^{-10}	4×10^{-10}	4×10^{-10}	4×10^{-10}	3×10^{-7}	3×10^{-7}	3×10^{-7}	3×10^{-7}
Initial Temp., Y	.02	.02	.02	.02	.02	.03	.03	.03	.03
Time Heat Flux Applied $\times 10^{-17}$	2.52	2.51	2.49	2.46	--	--	--	--	--
Time Heat Flux Applied $\times 10^{-11}$	--	--	--	--	--	8.04	7.92	7.68	7.02
Ratio, Delay	Cont.	~ 0	~ 0	$>10^1$	Cont.	~ 0	$>10^1$	$>10^1$	$>10^1$
Time to Time of Energy Application									

1. At end of computational period, the surface temperature was still decreasing rapidly.

TABLE NO. V

IGNITION DATA FROM HIGH TEMPERATURE,
ATMOSPHERIC FURNACE

Initial Propellant Temperature $28 \pm 1^\circ \text{C.}$

Propellant	Furnace Temp. $^\circ\text{K}$	Average Ignition Time, t_i , sec.	$t_i^{1/2}$ sec. $^{1/2}$	Furnace Flux cal/(sec)(cm 2)
F	1098	9.30	3.05	1.94
F	1304	3.24	1.80	3.86
F	1523	1.32	1.15	7.19
G	1098	13.15	3.64	1.94
G	1304	4.75	2.18	3.86
G	1523	2.15	1.47	7.19

TABLE NO. VI

SUMMARY OF THERMAL PROPERTIES

Except as noted all values are at 60° C.

Material	Density ² gr/cm ³	Heat Capacity cal/(gr)(°C)	Thermal		Thermal Conductivity cal/(sec)(cm)(°C)	Thermal Responsivity $\sqrt{k\rho c}$ cal/(sec) ^{1/2} (cm) ^{1/2} °C
			Diffusivity cm ² /sec	Conductivity		
Ammonium ¹ Perchlorate	1.95	0.256	2.22 x 10 ⁻³	1.106 x 10 ⁻³		2.35 x 10 ⁻²
A-Binder	1.24	0.428	0.93	0.531		1.85
F-Binder	1.11	0.424	1.055 1.002 ²	0.471		1.53
G-Binder	0.956	0.465	0.982 0.873 ²	0.437		1.39
A-Propellant	1.75	0.321	1.670	0.938		2.29
F-Propellant	1.63	0.316	1.700 1.731 ²	0.876		2.12
F-Propellant(MgO Modified)	1.64	0.308	1.674	0.846		2.07
G-Propellant	1.60	0.311	1.710 1.730 ²	0.851		2.06

1. The values for APC are at 20° C. The density value is from the International Critical Tables. The heat capacity value is from the JANAF Thermochemical Data; at 60° C. these data give a value of heat capacity of .275 cal/(gr)(°C).

2. These values are at 20° C.

TABLE NO. VII

SUMMARY OF TRANSIENT HEAT FLUX MEASUREMENTS
IN THE SEALED LOW-TEMPERATURE RADIATION FURNACE

Furnace Temp. °C	Furnace Press. atm	Total Heat Flux Btu/(sec)(ft ²)	Convective Heat Flux ¹		Convective Heat Transfer		Apparent Gage Absorptivity
			Btu/(sec)(ft ²)	Btu/(sec)(ft ²)	Btu/(hr)(ft ²)(°F)	Coefficient ²	
425	~0.03	1.09	--	--	--	--	0.92
424	0.85	1.36	0.27		1.4		
615	~0.03	2.43	--		--		.78
613	0.85	2.74	.31		1.1		
611	5.27	3.97	1.44		5.3		
613	9.15	5.04	2.61		9.6		
833	~0.03	5.10	--		--		0.68
829	0.85	5.34	.24		0.7		
829	5.44	6.05	.95		2.8		
833	9.00	6.61	1.51		4.4		

1. The convective flux was calculated as the observed flux less the measured flux under vacuum (.03 atm).

2. The solid to gas temperature difference was taken to be the observed value after about 10 seconds of exposure.

TABLE NO. VIII
COMPOSITIONS OF PROPELLANTS AND INGREDIENTS

<u>Material</u>	<u>Composition, weight per cent</u>
A-Binder	(polysulfide, polymer, etc.)
F-Binder	10 % Catalyst 13.5 % Epon Resin 828 (epoxy) 76.5 % Polybutadiene Acrylic Acid
F-Propellant	2 % Catalyst 2.7 % Epon Resin 828 (epoxy) 15.3 % Polybutadiene Acrylic Acid 80 % Ammonium Perchlorate (40% - 48 + 100 mesh; 40% ~ 40 micron)
F-Propellant - modified with MgO	0.14 % MgO 2 % Catalyst 2.7 % Epon Resin 828 (epoxy) 15.3 % Polybutadiene Acrylic Acid 79.86 % Ammonium Perchlorate
G-Binder	15 % Epon Resin 828 (epoxy) 85 % Polybutadiene Acrylic Acid
G-Propellant	2.7 % Epon Resin 828 (epoxy) 15.3 % Polybutadiene Acrylic Acid 82 % Ammonium Perchlorate (41% - 48 + 100 mesh, 41% ~ 40 micron)
I-Propellant	Same as G, except 41% - 32 + 100 mesh, 41% ~ 40 micron)
L-Propellant	2.4 % Epon Resin 828 (epoxy) 13.6 % Polybutadiene Acrylic Acid 84 % Ammonium Perchlorate (42% - 48 + 100 mesh, 42% ~ 42 micron)
Copper Chromite Catalyst	17 % Cr_2O_3 82 % CuO

TABLE OF NOMENCLATURE

A	constant in Equation (1)
B	constant in Equation (2)
B_2	constant in Equation (4)
C	constant in Equation (3)
c	propellant heat capacity per unit mass
D	ratio E_a/E_b
D_2	ratio AkE_b/RB^2
E	ratio E_c/E_b
E_2	ratio C/B
E_a	activation energy of solid reaction
E_b	activation energy of surface reaction
E_c	activation energy of surface reaction
F	dimensionless surface heat flux
f_s	surface heat flux
k	propellant thermal conductivity
m	constant in Equation (7)
N	number of time increments
R	gas constant
T	dimensionless time
U	dimensionless temperature
v	absolute temperature
X	dimensionless distance from the propellant surface
x	distance from the propellant surface
Y	dimensionless initial propellant temperature
α	thermal diffusivity of the material, $k/\rho c$
Γ	thermal responsivity of the propellant, $\sqrt{k\rho c}$

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